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PREPARATION OF LARGE-PARTICLE-SIZE MONODISPERSE LATEXES IN A ROTATING-CYLINDER REACTOR

J.H. Kim, E.D. Sudol, M.S. El-Aasser, J.W. Vanderhoff

Emulsion Polymers Institute and Departments of Chemical Engineering and Chemistry, Lehigh University, Bethlehem, Pennsylvania 18015 U.S.A.

and D.M. Kornfeld

George C. Marshall Space Flight Center, National Aeronautics and Space Administration, Huntsville, Alabama 35812 U.S.A.

ABSTRACT

The feasibility of preparing large-particle-size monodisperse latexes in a simulated microgravity environment was investigated using a rotating cylinder reactor. A rotational speed of 8 rpm was chosen for the polymerization of polystyrene particles in the size range of 6-60μm on the basis of results obtained in sedimentation studies. Improved particle-size uniformities were obtained when compared to more conventional polymerization techniques.

KEY WORDS

Monodisperse latex, simulated microgravity, rotating-cylinder reactor.

INTRODUCTION

The Monodisperse Latex Reactor (MLR) Space Processing Experiment has, thus far, successfully produced large-particle-size monodisperse polystyrene latexes in sizes of up to 30μm diameter in a microgravity environment (Vanderhoff *et al.*, 1984; 1987). This has been accomplished on four missions of the Space Shuttle. Three more flights are planned for producing latex particles in increasing size up to 100μm.

It is presently not easy to produce these large-size monodisperse latex particles on earth in usable quantities using standard emulsion polymerization techniques or equipment, due to buoyancy and sedimentation effects. During the early stages of the polymerization reaction, the large monomer-swollen latex particles tend to rise or "cream" to the surface of the reaction vessel because, during the first third of the reaction, the average density of the particles is less than that of the aqueous phase in which they are suspended (styrene monomer density = 0.905 g/cm^3). However, during the last two thirds of the reaction, the growing particles become denser as more monomer is converted to polymer (polystyrene density = 1.050 g/cm^3), and they tend to settle to the bottom of the vessel.

This tendency of the growing particles to first cream and then settle is not a significant problem for particle sizes below several micrometers in diameter, but as the particles are grown in successive seeding steps to diameters above 3μm, the rates of creaming and settling become so rapid that it is not possible to keep them in suspension using conventional stirrers and still maintain their stability. While the monomer-swollen particles are polymerizing, they are sticky and increasing the stirring rate causes more energetic particle-particle collisions, resulting in flocculation of the particles. Since it can be demonstrated experimentally that stirring the particles at rates high enough to prevent creaming or settling results in flocculation, a different method of agitation must be developed to produce these large-size particles.

The gravitational effects of creaming and settling can be eliminated by carrying out the polymerization in a microgravity environment (Vanderhoff *et al.*, 1984; 1987). In this case, the emulsifier concentration can be kept at a low enough level to ensure against new particle generation while maintaining the stability of the latex, and agitation would only be necessary to prevent significant temperature gradients within the polymerizing latex.

As a possible means to overcome the gravity effect and flocculation problem in preparing large-size latex particles on earth, application of a rotating reactor to the polymerization scheme will be explored. By using a reactor which is rotated horizontally about its long axis, the effective gravitational force on particles can be averaged to zero.

The gravity vector, rotating about its horizontally adjusted axis with a rotational frequency, ω, can be expressed following Equation (1).

$$G(t) = G_x\cos(\omega t) + G_y\sin(\omega t) \qquad (1)$$

$$\int_0^{\infty} G(t)dt = 0 \qquad (2)$$

Equation 2 indicates that the direction of the gravity vector rotates within the reaction chamber and its effect averages to zero over an extended period of time. Therefore, the gravity effect on any latex particle within the rotating reactor will be zero. In these expressions, centrifugal acceleration effects have been ignored. This is a good assumption at low rotational speeds. The latex particles will move in circular orbits inside the reactor; the diameter of the orbit is constant along the reactor radius vector and the period of the orbit coincides with the period of reactor rotation.

This principle has been applied successfully in the biological field with the propagation of small organisms by Miller (1959) and was developed extensively by Briegleb and Schatz (1973). In 1978, Otto and Lorenz proposed an experimental model of a rotating system and applied the above principle to the solidification of immiscible alloys.

The ultimate objective of this research effort is to determine whether the rotating-cylinder reactor can be used to grow monodisperse latex particles on earth to sizes larger than those currently possible in ground-based processes.

ROTATING-CYLINDER REACTOR

A rotating-cylinder reactor has been designed and constructed where the entire polymerization reaction chamber is rotated horizontally about its long axis while immersed in a constant temperature bath. This reactor is designed to maintain maximum uniformity in particle concentration and temperature with only a minimum amount of stirring, or possibly no stirring at all. The particles would be kept in suspension strictly through the rotation of the reactor, which is variable over a rpm range.

The rotating-cylinder reactor is basically a piston/cylinder dilatometer. It can be filled completely with a swollen latex eliminating any air-liquid interface. The variation of the latex volume as a function of temperature and degree of polymerization can be monitored continuously. A thermocouple is used to follow the latex temperature within the reactor. These data are recorded automatically on a 2-channel strip chart recorder.

A cut-away drawing of the rotating-cylinder reactor is shown in Figure 1. The mechanical aspects of the reactor system were designed to provide temperature control, fluid containment, and process measurements. The apparatus consists of a stainless-steel (SS) holder and glass cylinder (5.6 cm ID) in which rides a SS piston, sealed by two Viton O-rings. Piston movement is monitored by a linear variable differential transformer (type 250 HCD, Schaevetz Engineering) attached to the piston and fixed relative to the cylinder.

REACTOR EVALUATION

Several tests were devised and conducted in the rotating-cylinder reactor in order to determine the feasibility of using it to prepare large-particle-size monodisperse latexes. Temperature profiles and concentration gradients of sedimenting particles were used as measures of the efficiency of the apparatus during the development. Seeded polymerizations using large-size latex particles were performed using conditions based on the above findings.

Temperature Profiles

To determine whether significant temperature gradients existed in the rotating reactor under different operating conditions, five thermocouples were inserted through the opening normally used for the fluid temperature probe. The impeller was removed for these studies (i.e. no stirring was used). The thermocouples were arranged in two configurations: 1) vertically at the longitudinal center of the reactor, with the probes spaced evenly from the top to the bottom; and 2) horizontally along the axis of the reactor, displaced from the center and evenly spaced from one end to the other. The purpose of these configurations was to determine if convective currents were induced in the vertical direction and whether significant heat transfer occurred through the stainless steel at the reactor ends, respectively.

Temperature gradients were found during the heat-up period for the case where the thermocouples were oriented horizontally and the reactor was not rotated. These were attributed to the proximity of the thermocouple to the side plate which served as a heat sink. It took about 80 minutes to reach the steady state reaction temperature (70°C). Figure 2 shows that the top-to-bottom temperature gradients were 3°C or less in this extreme case. No significant vertical and horizontal temperature gradients were detected at various rotational speeds (4, 6, 8, & 10 rpm). These results are listed in Table 1.

Sedimentation Effects

The sedimentation of large-size latex particles at room temperature was studied as a function of time and velocity (rpm) of the rotating reactor. Poly(styrene-divinylbenzene) latexes,

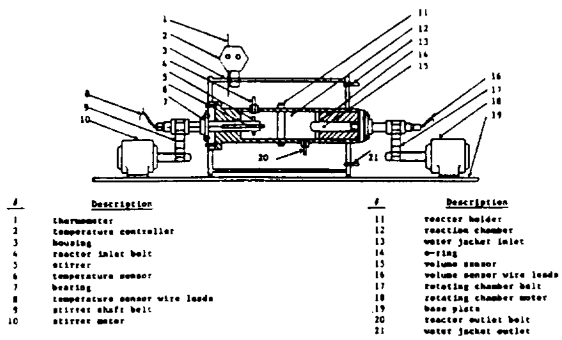

Fig. 1: Schematic diagram of the rotating-cylinder reactor.

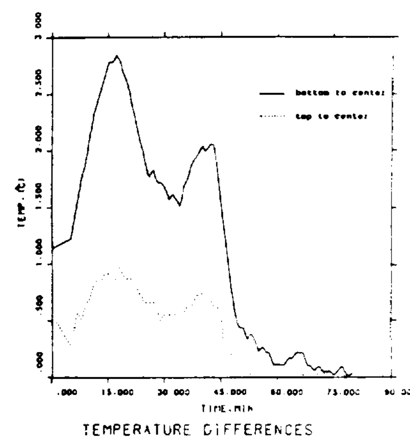

Fig. 2: Temperature gradients from top-to-center and bottom-to-center during heat-up period; no agitation or rotation.

TABLE 1
Maximum Temperature Differences (°C) in the Reaction Chamber at Various Rotational Speeds

Thermocouple Configuration	RPM 0	4	6	8	10
vertical	0.12	0.13	0.13	0.12	0.06
horizontal	0.09	0.15	0.09	0.04	0.03

having particle sizes of 26 ±6μm and 90 ±18μm (Dow Chemical Co.), were used. The sedimentation velocities of these particles were estimated to be the same as monomer-swollen particles of 28 and 96μm diameter (swelling ratio 6/1), respectively. Concentration gradients were measured by the relative amount (solids content) of latex particles found near the glass wall and the center of the polymerization chamber after rotating an originally well mixed system for a given time interval. Samples were removed via syringe at the two positions.

Some variation in the concentration of the 26μm particles was noted with time and rotational velocity (Figure 3). At the lowest rpm (4), the homogeneity of the suspension decreased with time; the decrease was less for 6 rpm, while, for 8 rpm and 10 rpm, the homogeneity increased after the first hour. These results show that a rotational velocity greater than 6 rpm is required to prevent inhomogeneities in this latex. The results obtained for the 90μm particles (Figure 4) clearly show that 4 and 6 rpm were inadequate in preventing concentration gradients in the rotating reactor; 8 rpm or higher was necessary to maintain homogeneity. However,

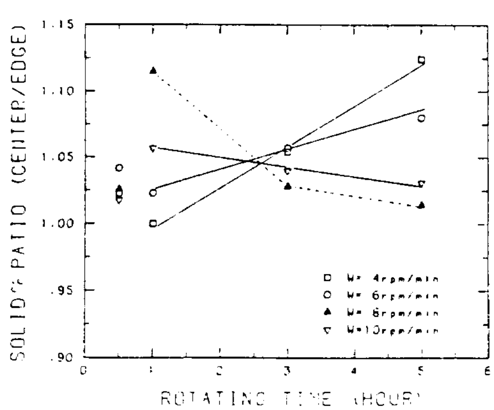

Fig. 3: Concentration gradients of 26μm polystyrene particles as a function of rotating time.

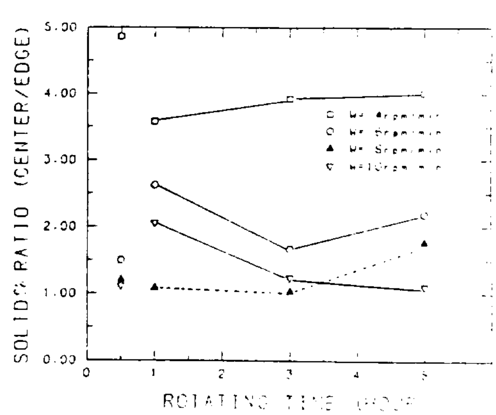

Fig. 4: Concentration gradients of 90μm polystyrene particles as a function of rotating time.

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visual observations showed that, even at these rotational speeds, the particles exhibited streaming patterns around the axis of the cylinder, which indicated that some sort of flow was set up under the conditions of the tests. Nonetheless, 8 rpm was chosen as the rotational speed to be used in subsequent polymerizations of large-particle-size latexes.

Successive Seeded Polymerizations

Based on recipe developments in the program to produce monodisperse latexes in microgravity (Vanderhoff *et al.*, 1984), six successive seeding experiments were run in the rotating-cylinder reactor in an attempt to further investigate the feasibility of preparing large-particle-size latexes of narrow size distribution.

The seed used in the first step of this sequence of experiments was a monodisperse 3.4μm polystyrene latex. The second seeding step used the product of the first as the seed and so on. The water was distilled and deionized (DDI). Table 2 lists the initiators, buffers, and inhibitors used in these studies along with the corresponding manufacturers. Typical recipes for the preparation of large-particle-size latexes in the rotating cylinder reactor are given in Table 3. 300 grams of each recipe was prepared for loading the reactor. Specified amounts of emulsifier, DDI water, latex seed, monomer, buffer, initiator, and inhibitor were weighed into a 16 oz. bottle. Swelling was accomplished in 24 hours at room temperature by rotation of the bottle at 32 rpm about its horizontal axis.

TABLE 2
Initiator, Buffer, Inhibitor

Chemical	Manufacturer	Purity
$K_2S_2O_8$	Fisher Scientific Co.	recrystallized from DDI water
AMBN*	VA3607 DuPont Co.	recrystallized from isopropanol
$NaHCO_3$	Fisher Scientific Co.	certified A.C.S.
Hydroquinone	Fisher Scientific Co.	"purified"
Benzoquinone	Fisher Scientific Co.	"purified"

* azobis-(2-methyl-butyronitrile)

TABLE 3
Polymerization Recipes*

	Recipes S-1 to S-5	S-6
AMBN	0.2	0.1
PVP K-90†	2.5	2.5
KX-3‡	0.032	0.032
Divinylbenzene	0.310	0.310
Hydroquinone	0.085	0.085
Benzoquinone	0.015	0.015
Styrene	100.0	100.0
Solids Content	30%	10%
Monomer/Polymer	5/1	5/1

* based on 100 parts monomer
† polyvinylpyrrolidone (GAF)
‡ Polywet anionic surfactant (Uniroyal)

The swollen latex was first filtered through glass wool to remove any viscous material which may have formed during the swelling. The latex was then degassed at a pressure of 20 mm Hg via aspirator until bubble formation had ceased. This degassed latex was then loaded into the reactor with any air being expelled during the process. The bath temperature had already been adjusted to the polymerization temperature (70°C) prior to this operation.

Once loaded, the piston position was monitored to check for possible leaks after which the motor controlling the reactor rotation was switched on. The rotational speed used in all of these experiment was 8 rpm. No additional agitation was used. The polymerization was monitored until completed as indicated by cessation of piston movement.

Scanning Electron Microscopy was used to obtain a qualitative estimation of the monodispersity and relative number of off-size particles in a latex sample.

Six successive seeding experiments were conducted using AMBN initiator. The step-by-step particle sizes were:

$$3.4\mu m \rightarrow 6.8\mu m \rightarrow 9.8\mu m \rightarrow 14.5\mu m \rightarrow 25.5\mu m \rightarrow 43.4\mu m \rightarrow 59.6\mu m$$

Scanning electron micrographs of each product are presented in Figure 5. Particle size distributions were also determined and are shown in Figure 6. These results indicate that the size distributions of these products are as narrow as the original seed latexes. However, all

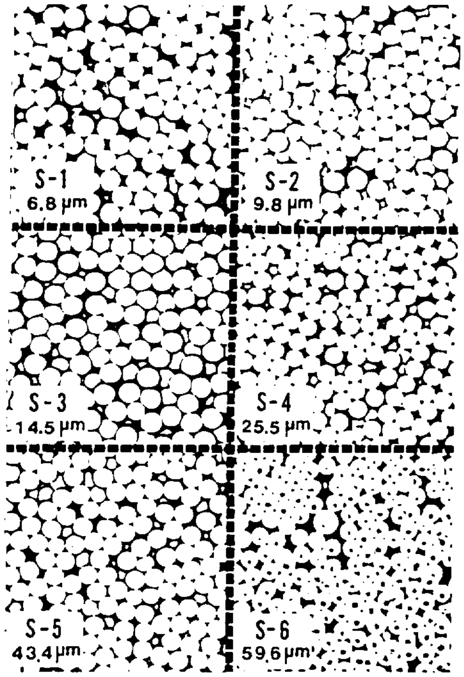

Fig. 5: Scanning Electron Micrographs of S-Series latex particles.

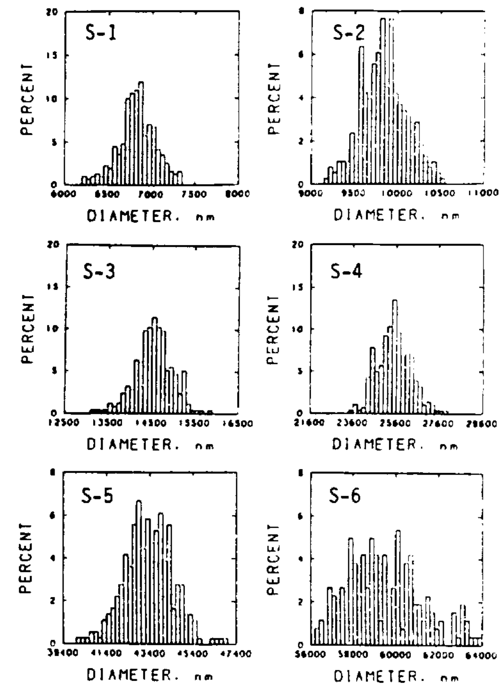

Fig. 6: Particle Size Number Distributions of S-Series latex particles.

of these latexes contained small amounts of off-size particles which were significantly larger or smaller than the main distribution. Table 4 gives the relative numbers of these off-size particles. The number of off-size and odd shaped particles increased with increasing size particularly from the fifth step (particle size above 40μm in diameter). These large off-size particles are attributed to the coalescence of two or more monomer swollen seed particles or to the presence of a few off-size particles in the seed latex which grew proportionately during the sequential polymerization. The uniformity, expressed by Δ/D_n and D_w/D_n, is also given in Table 4. D_n is the number average diameter, D_w the weight average diameter and Δ the standard deviation. The polydispersity index, D_w/D_n, was about the same for all latexes, but the uniformity expressed as the absolute value of Δ increased with increasing particle size from 0.22 for the S-1 latex to 1.76 for the S-6 latex.

Table 4
Particle Size Distributions

Sample	D_n, μm	Δ, μm	Δ/D_n, %	D_w/D_n	Off-Size Particles*
S-1	6.83	0.22	3.16	1.003	1/311
S-2	9.84	0.26	2.68	1.002	1/320
S-3	14.56	0.44	2.99	1.003	1/257
S-4	25.50	0.77	3.03	1.003	1/249
S-5	43.35	1.14	2.62	1.002	1/105
S-6	59.55	1.76	2.95	1.003	1/47

* relative to the main distribution

Coagulum levels decreased with increasing particle size in the first three steps. After this, none of the polymerizations produced significant amounts of coagulum. This was attributed to an increase in the amount of polymeric stabilizer in the latex. One problem which may have reduced the effectiveness of the reactor was the formation of gas bubbles which increased in size throughout the reaction. This was due in part to the evolution of nitrogen from decomposition of the initiator. Degassing the swollen latex reduced the size of the bubbles, but they were only eliminated when the initiator concentration was reduced by decreasing the recipe solids from 30% to 10% (step 6).

Simultaneous polymerizations were carried out in the rotating-cylinder reactor and a 16 oz. (473 cm^3) bottle using the same recipe of step S-6. Figure 7 shows a scanning electron micrograph of the bottle polymerization product. The polydispersity of this latex is due to the flocculation of the newly generated small particles and the monomer-swollen seed particles caused by the more severe agitation conditions.

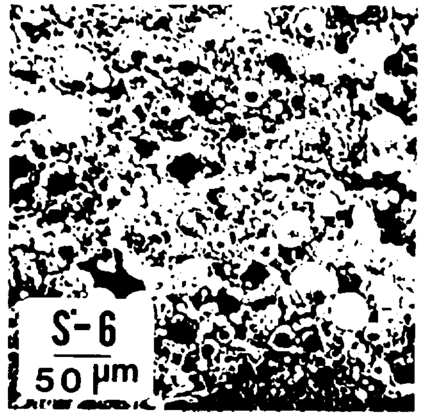

Fig. 7: Scanning Electron Micrograph of the bottle polymerization products based on S-6 recipe

SUMMARY

Using a rotating-cylinder reactor in successive seeded polymerizations effectively eliminates the gravitational effects of creaming and settling, leading to the successful preparation of large-particle-size monodisperse particles with diameters of up to 60μm. Improvements in the seeded emulsion polymerization recipes are foreseen and thereby, improvements in the latexes prepared in the rotating-cylinder reactor.

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